

FORM-PTO-1390 (Rev. 9-2001)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				004900-214
INTERNATIONAL APPLICATION NO. PCT/FR00/02610		INTERNATIONAL FILING DATE 20 SEPTEMBER 2000		U.S. APPLICATION NO. (If known, see 37 C.F.R. 1.5) 104088234 UNASSIGNED
TITLE OF INVENTION COMPOSITION USEFUL FOR CONDITIONING SLUDGE DERIVED FROM THE TREATMENT OF AN AQUEOUS MEDIUM AND USES THEREOF				PRIORITY DATE CLAIMED 20 SEPTEMBER 1999
APPLICANT(S) FOR DO/EO/US Yvette PESCHER; Bruno BAVOUZET and Michele RAFFARD				
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:				
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input type="checkbox"/> have not been made and will not be made. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). 				
Items 11 to 20 below concern document(s) or information included:				
<ol style="list-style-type: none"> <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. <input type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. <input type="checkbox"/> A substitute specification. <input type="checkbox"/> A change of power of attorney and/or address letter. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). <input checked="" type="checkbox"/> Other items or information: 				
Form PCT/IB/304; Form PCT/RO/101 (PCT Request); Form PCT/IPEA/416; Form PCT/IPEA/409 (Preliminary Exam. Report); Form PCT/ISA/220; Form PCT/ISA/210 (Search Report) and Four (4) Sheets of Drawings.				



21839

U.S. APPLICATION NO. (If known, see 37 CFR 1.15)	INTERNATIONAL APPLICATION NO.	ATTORNEY'S DOCKET NUMBER
UNASSIGNED 107088234	PCT/FR00/02610	004900-214
21. <input checked="" type="checkbox"/> The following fees are submitted:		CALCULATIONS
Basic National Fee (37 CFR 1.492(a)(1)-(5)):		
Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1,040.00 (960)		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 (970)		
International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 (958)		
International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 (956)		
International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 (962)		
ENTER APPROPRIATE BASIC FEE AMOUNT =		\$ 890.00
Surcharge of \$130.00 (154) for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492(e)).		20 <input type="checkbox"/> 30 <input type="checkbox"/>
Claims	Number Filed	Number Extra
Total Claims	-20 =	X\$18.00 (966)
Independent Claims	-3 =	X\$84.00 (964)
Multiple dependent claim(s) (if applicable)		+ \$280.00 (968)
TOTAL OF ABOVE CALCULATIONS =		\$ 890.00
Reduction for 1/2 for filing by small entity, if applicable (see below).		+ \$
SUBTOTAL =		\$ 890.00
Processing fee of \$130.00 (156) for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492(f)).		20 <input type="checkbox"/> 30 <input type="checkbox"/>
TOTAL NATIONAL FEE =		\$ 890.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). \$40.00 (581) per property		+ \$
TOTAL FEES ENCLOSED =		\$ 890.00
		Amount to be refunded: \$
		charged: \$
a. <input type="checkbox"/> Small entity status is hereby claimed.		
b. <input checked="" type="checkbox"/> A check in the amount of \$ <u>890.00</u> to cover the above fees is enclosed.		
c. <input type="checkbox"/> Please charge my Deposit Account No. <u>02-4800</u> in the amount of \$ _____ to cover the above fees. A duplicate copy of this sheet is enclosed.		
d. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. <u>02-4800</u> . A duplicate copy of this sheet is enclosed.		
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.		
SEND ALL CORRESPONDENCE TO:		
Norman H. Stepmo, Esq. BURNS, DOANE, SWECKER & MATHIS, L.L.P. P.O. Box 1404 Alexandria, Virginia 22313-1404 (703) 836-6620		
SIGNATURE		TERESA STANEK REA
NAME		MARCH 19, 2002
30,427 REGISTRATION NUMBER		DATE

Rec'd PCT/PTO 07 JUN 2002

WO 01/21532

PCT/FR00/02610

COMPOSITION USEFUL FOR CONDITIONING SLUDGE FROM THE
TREATMENT OF AQUEOUS MEDIA AND USES THEREOF

5

The present invention concerns a novel composition which can be used in particular for treating aqueous media such as waste or urban or industrial water and more particularly conditioning sludge prior to the operation for dehydration thereof.

10

The treatment of waste, urban or industrial water, in particular by a biological method, in purification stations, results in the production of sludges. Those sludges are generally subjected to a mechanical dehydration operation (in particular filtration or centrifuging) before being transported to a discharge site, an agricultural spreading site or an incineration site.

15

The sludges to be treated are formed for the major proportion thereof by water in which the biomass is dispersed in a proportion of between 12 and 40 g/l. The treatments therefore aim at providing for maximum concentration of the dry matter and eliminating the water.

20

The object of the present invention is precisely to propose a novel composition which can be effectively used in conditioning this type of sludge, making it possible in particular to increase its dryness, that is to say to increase the dry extracts obtained in the subsequent dehydration operation.

25

When the sludge is intended for a filter press, an inorganic salt associated if appropriate with an electrolyte, generally lime, is conventionally added to the sludge to be treated.

30

On the other hand when the sludge is intended to be treated on a belt filter or by means of a centrifuge, the drainability necessary for removal of the water is generally achieved by sequentially adding thereto an inorganic salt, a cationic polymer and then optionally an anionic polymer.

The methods of treating sludges which are available at the present time are therefore different, according to the water/biomass separation procedure adopted. On the other hand, they generally necessitate the successive addition of a plurality of reactants. It is in fact found to be

difficult to formulate in a single composition and at significant levels of concentration, an organic salt of polyaluminum chloride type and a cationic polyelectrolyte. Aluminum being a sequestering agent in respect of certain polyelectrolytes, the mixtures thereof result, from a certain level of 5 concentration in respect of such compounds, in the formation of gels which as will be appreciated are prejudicial in terms of fluidity to the corresponding mixtures.

The object of the present invention is precisely to propose a universal composition, that is to say which can be used equally for treating sludges 10 according to either one of the above-discussed procedures.

Moreover the claimed composition affords the advantage of combining in the form of a mixture, a mineral cation of a charge of higher than or equal to 2 and a cationic polyelectrolyte, while not being subject to the above-discussed gelling phenomenon.

15 More precisely, the main object of the present invention is a composition which is useful for conditioning sludge obtained by mixing at least one invert emulsion containing at least one cationic polyelectrolyte with an invert emulsion or an aqueous solution containing at least one mineral cation with a charge of higher than or equal to two.

20 The invention also extends to a composition which is useful for conditioning sludge characterised in that it is in the form of an emulsion comprising in an aqueous phase or phases and separately at least one mineral cation with a charge of greater than or equal to 2 and a cationic polyelectrolyte.

25 In accordance with a first embodiment the composition is in the form of an invert water-in-oil emulsion in which the mineral cation and the cationic polyelectrolyte are distributed in water droplets which are distinct in the oily phase.

This type of composition is generally obtained by mixing with 30 agitation an invert emulsion containing the mineral cation with an invert emulsion containing the cationic polyelectrolyte.

In accordance with a second embodiment the composition is in the form of a double water/oil/water emulsion in which the mineral cation is

present at the level of the continuous aqueous phase and the cationic polyelectrolyte is distributed at least in part in water droplets constituting the second aqueous phase dispersed in the oily phase.

This second type of emulsion can be obtained by mixing an invert emulsion of the cationic polyelectrolyte with an aqueous solution of the mineral cation.

The compositions claimed are particularly advantageous insofar as they are found to be effective for all of the procedures for treating sludges, namely belt filtration and/or centrifuging or filtration on a press.

Moreover, by permitting isolation of the mineral cation from the cationic polyelectrolyte, they make it possible to formulate those reactants in higher concentrations. By virtue of that formulation in emulsion, the risk of gelling is significantly reduced.

The composition obtained by mixing the two invert emulsions, namely that of the mineral cation and that of the cationic polyelectrolyte, is more particularly suited to the formulation of a concentrated composition. In fact, those two compounds are then distributed at the level of the emulsion in separate water droplets and are therefore effectively isolated from each other.

The mineral cation has a charge of greater than or equal to 2. It is usually selected from Mg^{2+} , Al^{3+} , Fe^{3+} , La^{3+} , Zr^{4+} and their polymerised forms when they exist. Very preferably, the cation is Al^{3+} or one of its polymerised forms.

That mineral cation is present in the form of a water-soluble salt. As soluble salts, it is possible to use chlorides, nitrates, sulfates and acetates.

In general, the procedure involves using a soluble salt which is free from the element nitrogen, which makes it possible to avoid possible problems linked to the presence thereof. Very preferably, a chloride is used. The cation is preferably an aluminum chloride or one of its polymerised forms and more preferably polyaluminum chloride.

The amount of mineral cation used is preferably between 0.05 and 2 moles, in particular between 0.49 and 1.8 moles per kg of the composition.

The pH-value of the solution or emulsion is adjusted in such a way as to prevent precipitation of the mineral salt in the continuous aqueous phase. That adjustment is a matter for the capability of the man skilled in the art.

5 As regards the cationic polyelectrolyte it is preferably of high molecular weight, that is to say of a molecular weight of greater than 1.10^6 .

The polyelectrolytes are preferably of a molecular weight of between 1.10^6 and about 20.10^6 , more preferably between 1.10^6 and about 10.10^6 .

10 The cationic polyelectrolyte can be branched or straight-chain and is preferably in branched form. It has in fact been noted that the branchings have a beneficial effect on the coagulation and flocculation kinetics.

15 Particularly suitable cationic polyelectrolytes are polyacrylamides, oxides of polyethylenes and polyvinylpyrrolidones, as well as polymers of natural origin such as starch and derivatives thereof or gum such as gum guar, insofar as they are cationic.

Preferably the polyelectrolyte is a polyacrylamide.

The polyacrylamide can be cationic up to 100% in respect of charge and is preferably cationic at between about 0.1 and 15% in respect of charge.

20 The cationic polyacrylamides comprise copolymers of polyacrylamide with cationic monomers or polyacrylamides modified in accordance with the Mannich reaction.

25 The examples of cationic polyacrylamide copolymers include the copolymers acrylamide/halide and preferably chloride of diallyldialkylammonium, the copolymers diaminoalkylmethacrylate/acrylamide and the copolymers dialkylaminoalkylmethacrylates/acrylamides, the alkyl group being C₁ to C₆.

30 Advantageously the cationic polyelectrolyte is a polyacrylamide copolymer and preferably the copolymer polyacrylamide/diallyldimethylammonium chloride of a molecular weight of the order of 3.10^6 . It is more preferably associated with an polyaluminum chloride in the composition claimed.

The amount of cationic polyelectrolyte present in the composition claimed is preferably at most 10% by weight, in particular between 0.3% and 8% by weight of said composition.

Generally the invert emulsion of the cationic polyelectrolyte, for example in the case of a polyacrylamide of high molecular weight and the aqueous solution or the invert emulsion of the mineral cation, for example in the case of the polyaluminum chloride, are used in such a way that the molar ratio (mineral cation with a charge of greater than or equal to 2)/(cationic polyelectrolyte) is between 1.10^2 and 8.10^6 and in particular between 1.10^3 and 8.10^6 . In the particular case of a composition comprising polyaluminum chloride and a copolymer acrylamide/diallyldialkylammonium chloride of high molecular weight, the weight ratio of polyaluminum chloride/polyacrylamide used is preferably between 0.1 and 15 and more particularly between 0.1 and 10.

As indicated hereinbefore the compositions claimed containing the mineral cation and the cationic polyelectrolyte which are distributed in separate water droplets in the continuous oily phase are particularly attractive in terms of formulating a composition which is concentrated in respect of those two compounds. It is thus that this mode of formulation will be afforded the preference for compositions containing a concentration of polyacrylamide of the order of between 4 and 10% by weight with respect to the composition.

If necessary the composition claimed can be stabilised in the form of an emulsion by means of a surface active agent or agents. The surface active agents are generally introduced at the level of the invert emulsion or emulsions constituting the composition.

As regards the surface active agent which is present in the oily phase of the emulsion, this is preferably a surface agent which as will be appreciated remains inert in relation to the mineral cation.

The liposoluble surface active agents which can be used in the emulsion according to the invention can be selected from liposoluble lecithins, esters of sorbitan and fatty acids, polyalkylene

dipolyhydroxystearates, fatty acids, monoglycerides, polyglycerol esters and esters of lactic and tartric acids.

By way of illustration of the water-soluble surface active agents, mention may be made in particular of water-soluble lecithins, sucrose esters, fatty acid esters (including Tweens®), polyoxyethylenated alkylamides, triglyceride sulfates, alkyl sulfates (including sodium dodecyl sulfate SDS), alkyl ether sulfates, alkyl sulfonates, alkylamine salts, fatty amines, lipoamino acids, modified polyesters and silicone-bearing polymeric surface active agents.

10 The amounts of surface active agents are adjusted in such a way as to stabilise the formulation (invert or double emulsion) of the composition.

The composition claimed can be prepared either by mixing the two invert emulsions respectively containing the mineral cation and the polyelectrolyte, or by adding the invert emulsion containing the 15 polyelectrolyte to an aqueous solution of the polyelectrolyte. The mixtures are generally produced at ambient temperature and with adequate mechanical agitation to result in an emulsion which is stabilised in respect of time.

By way of illustration of the compounds which are suitable for use as 20 the oily phase in accordance with the invention, mention may be more particularly made of hydrophobic materials such as in particular rosin esters, lanolin, vaseline, waxes, polybutadienes of low molecular masses, animal, vegetable or mineral natural oils and mixtures thereof.

The compositions claimed are used in a particularly attractive manner 25 in the chemical conditioning of sludge, in particular sludge coming from purification stations for treating dirty or waste or urban or industrial water: the incorporation thereof into the sludge, which can be subjected beforehand to an anaerobic digestion treatment, makes it possible to structure same in such a way that the water contained in the sludge is best 30 exudated in the dehydration operation which follows. The effectiveness of the mechanical dehydration operation such as filtering or centrifuging can thus be improved, the volumes produced after that dehydration procedure

being reduced by virtue of obtaining a filter cake with a high level of dryness.

The amount of composition used for conditioning a sludge is such that it generally corresponds to between 0.05 and 3 times and preferably 5 between 0.1 and 2 times the amount of theoretical cationic charge necessary to neutralise the amount of cationic charge of the sludge to be treated; in other words, the amount of composition claimed is such that as an absolute value it has a cationicity generally equal to between 0.05 and 3 times and preferably between 0.1 and 2 times the anionicity of the sludge 10 to be treated.

In general the compositions claimed are diluted before use. That dilution is more particularly necessary for the composition which occurs in the form of an invert emulsion obtained by mixing the invert emulsion of the mineral cation and that of the polyelectrolyte for transforming it into a 15 direct emulsion. That phase inversion can also be implemented by adding a suitable surface active agent. In the case where the compositions are in the form of double emulsions the dilution operation on the other hand is optional.

The following Examples and Figures are set forth by way of non- 20 limiting illustration of the invention.

FIGURES

Figure 1: representation for composition A and for its constituents when added separately, of the evolution in the volume drained at the end of 2 minutes in dependence on the conditioning dose.

25 Figure 2: representation for composition B and for its constituents when added separately, of the evolution in the volume drained at the end of 2 minutes in dependence on the conditioning dose.

Figure 3: representation of the graph showing t/v in dependence on v for the composition A and its constituents when added separately.

30 Figure 4: representation of the graph showing t/v in dependence on v for the composition B and its constituents when added separately.

Abbreviations:

PAM - cationic polyacrylamide

PAC - polyaluminum chloride

Material

Invert emulsion of copolymer acrylamide/diallyldialkylammonium chloride of a molecular weight of about 3.10^6 , as 50% by weight, referred 5 to hereinafter as 'PAM emulsion'.

Copolymer acrylamide/diallyldimethylammonium chloride of molecular weight of about 3.10^6 in powder form.

Aquarhone 18[®] (solution of polyaluminum chloride marketed by Rhodia containing 4.56 moles of aluminum per kg - E.S = 38.2%).

10 Vaseline (Prolabo)

Alkamuls S80[®]: sorbitan oleate of HLB 4.3 (Rhodia).

Alkamuls S20[®]: sorbitan monolaurate of HLB 8.6 (Rhodia)

Span 85[®]: sorbitan trioleate of HLB 1.7 (Sigma-Aldrich)

Alkamuls T20[®]: sorbitan monolaurate of 200E HLB 16.6 (Rhodia)

15 Alkamuls T85[®]: sorbitan trioleate 200E HLB 11 (Rhodia)

Ethoxylated phosphate esters PA35 (Rhodia).

EXAMPLE 1:

Producing an invert emulsion of PAM.

Diallyldimethylammonium chloride of a molecular weight of about 20 3.10^6 .

Taking 50 g of cationic polyacrylamide copolymer in the form of a powder, an invert emulsion is produced in a water/vaseline 1g/47.4 g mixture using 1.6 g of a mixture of sorbitan monolaurate/sorbitan oleate S20/S80 88%/12% (that is to say the required HLB of 8 for vaseline).

EXAMPLE 2:

Producing an invert emulsion of PAC.

a) A solution, Aquarhone 18[®], is diluted with water (20g of water for 50g of Aqua 18).

b) 5% of surface active agent S80[®] is added to the vaseline oil (that 30 is to say 2g of S80 for 38g of vaseline).

After passing b) for a period of 30s in an utraturax at 8000 rpm, a) is progressively poured into b) for a period of about 5 minutes, still at the same speed. Addition is effected for one minute at a speed of 9500 rpm.

After storage for one week at 45°C, those emulsions whose size is less than 5 µm experience slight sedimentation (appearance of a small amount of supernatant oil). The whole thing however is fairly easily returned to solution by simple manual agitation.

5 **EXAMPLE 3:**

Production of an invert PAC-PAM emulsion.

Using an ultraturax, 92.35g of the PAC emulsion prepared in accordance with Example 2 and 7.6g of the PAM emulsion prepared in accordance with Example 1 are mixed.

10 That then gives a fluid invert emulsion comprising by weight: 16.1% of PAC, 3.8% of PAM, 42.8% of water, 35.7% of oil and at least 1.6% of surface active agent.

The different tests carried out show that mixing using the ultraturax of the two invert emulsions obtained in accordance with the preceding
15 Examples makes it possible to obtain an invert PAC-PAM emulsion whose behaviour in respect of stability is similar to the invert emulsions of PAC alone.

Inversion of a PAC-PAM emulsion preserved for 13 days and then re-homogenised is achieved after the addition of a surface active agent such
20 as sorbitan monolaurate 200E Alkamuls (T20®) in water. As soon as that emulsion is direct again, the viscosity of the system increases greatly and demonstrates the formation of the gel polyacrylamide Al³⁺. That observation indicates limited diffusion of PAM or PAC between the drops of water during the storage period.

25 The two compounds are thus effectively separated within the invert emulsion, thus preserving for same a satisfactory level of fluidity.

EXAMPLE 4:

Preparation of a double emulsion based on PAC and PAM.

This emulsion is prepared by mixing an aqueous solution of
30 polyaluminium chloride (commercial solution Aquarhone 18®) and an invert PAM emulsion.

The invert PAM emulsion is prepared in accordance with the procedure described hereinbefore in Example 1. It is then added with

agitation to Aquarhone 18®. Two mixtures A and B are thus obtained with different PAC/PAM ratios.

- for a mixture referred to as A: a commercial emulsion of PAM with 4% and a solution of Aquarhone 18® are mixed, in such a way as to 5 produce a mixture with 18.2% of commercial Aquarhone 18® and 3.27% of PAM emulsion, being a weight ratio of PAC/PAM active materials of 3.9;

- for a mixture referred to as B: a commercial emulsion of PAM with 2% and a solution of Aquarhone 18® are mixed, in such a way as to produce a mixture with 20% of commercial Aquarhone 18® and 1.6% of 10 PAM emulsion, being a weight ratio of PAC/PAM active materials of 8.75.

The effectiveness of the mixtures A and B is evaluated in drainability and piston filter tests and compared to that obtained with sludges into which Aquarhone 18® and the PAM emulsion have been incorporated separately and sequentially, in amounts identical to those involved in the 15 respective mixtures.

EXAMPLE 5:

Drainability test.

This involves a test which makes it possible to identify the composition which is more particularly suitable for dehydration of the 20 sludges on a belt filter and/or a centrifuge.

This test is carried out on 200g of biological sludge from an urban purification station having a proportion of dry matter of 6.35% of which 37.2% is mineral materials.

a) With the mixture A and its reference (separate and sequential 25 addition of the two constituents)

In the tests A is diluted to 1/6th, which provides that the amount of Aquarhone 18® goes from 18.2 to 3.03% and the amount of PAM emulsion goes from 3.27 to 0.545%.

Consequently, the respective amounts of the comparison 30 constituents, that is to say which are added separately, are appreciated as follows:

- corresponding to 10g of A at 1/6th (that is to say 1.67g of pure A) there are 0.303g of commercial Aquarhone 18® and 9.7g of PAM emulsion.

In the case of the drainability test with emission A, the latter is added to 200g of sludge with mechanical agitation with a lacerating blade at 700 rpm in a beaker, the mixture is then poured into a filter and the amount of water which has percolated in dependence on time is evaluated.

5 In the case of the comparison drainability test, the procedure involves the sequential addition of the two products in accordance with the following mode of operation:

10 200g of sludge is agitated at 700 rpm. Aquarhone E 18[®] is added thereto and agitation is continued for 10 seconds. The pre-conditioned sludge is then poured into a beaker in which the PAM emulsion has been weighed beforehand. The whole is poured twice from one beaker to another and then agitated for 15 seconds at 700 rpm. It is then deposited on a filter and the amount of water percolated is measured.

15 The results obtained with A and the comparison are presented in the form of graphs in Figure 1.

b) Mixture B and comparison mixture

In the tests B is diluted to 1/3rd, which means that the amount of Aquarhone 18[®] goes from 20.0% to 6.67% and the amount of PAM emulsion goes from 1.6% to 0.53%.

20 Thus 10g of B at 1/6th (that is to say 3.33g of pure B) corresponds to 0.667g of commercial Aquarhone 18[®] and 9.33g of PAM emulsion to 0.57%.

25 The addition of emulsion B and the addition of its two constituents separately in the comparison test is carried out in accordance with the procedures described for the preceding test.

The results obtained with B and its comparison are set out in the form of graphs in Figure 2.

30 The array of the graphs in Figures 1 and 2 gives, for the mixtures A and B and for their constituents when added separately, the volume drained at the end of 2 minutes in dependence on the conditioning dose. It will be noted that the conditioning operations effected by the addition of Aquarhone 18[®] and then the PAM emulsion give smaller drained volumes than in the case of the conditioning operations which are implemented on

the basis of the mixtures A and B. In consequence, use of the mixtures permits an economy in terms of product of between 20 and 40% with respect to the constituents when added separately, while maintaining optimum effectiveness.

- 5 Moreover the mixtures A and B are found to be markedly less viscous than the 0.56% PAM solution.

EXAMPLE 6

Evaluation on a piston filter.

- This involves a test which makes it possible to identify the
10 compositions which are more particularly suitable for dehydration of the sludge on a filter press.

This test is carried out with the following filtration conditions:

- 100g of conditioned sludge is filtered on a piston filter at 2.10^5 Pascals for a period of 10 minutes in order to plot the time/volume graph
15 (T/V) in dependence on the volume which makes it possible to demonstrate the behaviour upon filtration. A filtration operation is then effected at 1.10^6 Pascals for a period of 5 minutes in order to estimate the influence of the different conditioning procedures on the limit dryness obtained.

- The conditioning dose is determined by measuring the capillary
20 suction time (CST) at different doses.

Two doses for the conditioning operations are adopted: the dose at the minimum CST time and the dose with a slight overdosing.

a) Mixture A and its comparison

Results with A diluted to 1/6th.

- 25 The conditioning doses are determined by measuring the CST. The data obtained are set forth in Table I hereinafter.

TABLE I

CST on 50g of sludge	dose A 4% 1/6th (g)	CST (sec)
	2.5	>600
	3.00	24.60
	3.50	17.50
	4.00	31.00

The doses adopted are as follows:

- 3g of A at 1/6th for 50g of sludge, and
- 3.5g of A at 1/6th for 50g of sludge.

5 The filtration test is then carried out on a piston filter in accordance with the procedure described hereinbefore. The results obtained are presented in graph form in Figure 3.

Figure 3 also shows in graph form the results obtained for a sludge treated successively with the two constituents of A when added separately.

10 The doses of those constituents are calculated in the same manner as for the drainability test set out in Example 5.

b) Mixture B and its comparison

In the same manner as for mixture B, the doses in respect of A are determined by measurements of CST at different doses. They are set out in
15 Table II below.

TABLE II

CST on 50g of sludge	dose B 2% 1/3rd	CST (sec)
	1.50	272.0
	2.00	19.10
	2.50	20.50
	3.00	18.50
	4.00	44.10

The doses adopted are 2g of B at 1/3rd for 50g of sludge and 3g of B at 1/3rd for 50g of sludge.

20 Filtration tests are then carried out on the piston filter using the procedure as described hereinbefore.

The results obtained with emulsion A and its comparison mixture and likewise emulsion B and its comparison mixture are respectively set forth in Figures 3 and 4. Those Figures show the graphs in respect of t/v in
25 dependence on v for the two mixtures and their constituents when added separately. It appears that it is in terms of dryness or in terms of behaviour

upon filtration that the fact of adding the products constituting the mixtures separately reduces the effectiveness of the conditioning procedure. The specific resistances are in fact higher and the levels of dryness lower.

CLAIMS

1. A composition useful for conditioning sludge obtained by mixing at least one invert emulsion containing at least one cationic polyelectrolyte with an invert emulsion or an aqueous solution containing at least one mineral cation with a charge of greater than or equal to two.
2. A composition useful for conditioning sludge characterised in that it is in the form of an emulsion comprising in aqueous phase or phases and separately at least one mineral cation of a charge of greater than or equal to 2 and a cationic polyelectrolyte.
3. A composition as set forth in claim 1 or claim 2 characterised in that it is in the form of an invert water-in-oil emulsion in which said mineral cation and said cationic polyelectrolyte are distributed in separate water droplets in the oily phase.
4. A composition as set forth in claim 1 or claim 2 characterised in that it is in the form of a double water/oil/water emulsion in which the mineral cation is present at the level of the continuous aqueous phase and the cationic polyelectrolyte is distributed at least in part in water droplets constituting the second aqueous phase which is dispersed in the oily phase.
5. A composition as set forth in one of the preceding claims characterised in that the mineral cation is selected from Mg^{2+} , La^{3+} , Fe^{3+} , Al^{3+} , Zr^{4+} and their polymerised forms when they exist.
6. A composition as set forth in claim 5 characterised in that said mineral cation is Al^{3+} or one of its polymerised forms.
7. A composition as set forth in one of the preceding claims characterised in that the mineral cation is in the form of a water-soluble salt selected preferably from chlorides, nitrates, sulfates and acetates.

8. A composition as set forth in one of the preceding claims characterised in that the mineral cation is an aluminum chloride or one of its polymerised forms.

9. A composition as set forth in one of the preceding claims characterised in that the mineral cation is used in a proportion of between 0.05 and 2 moles, in particular between 0.49 and 1.8 moles per kg of said composition.

10. A composition as set forth in one of the preceding claims characterised in that the cationic polyelectrolyte is of a molecular weight of higher than 1.10^6 .

11. A composition as set forth in one of the preceding claims characterised in that the cationic polyelectrolyte is selected from polyacrylamides, oxides of polyethylenes, polyvinylpyrrolidones, and cationic polymers of natural origin.

12. A composition as set forth in one of the preceding claims characterised in that said cationic polyelectrolyte is a polyacrylamide having between 0.1% and 15% of cationic charge.

13. A composition as set forth in one of the preceding claims characterised in that the cationic polyelectrolyte is selected from copolymers of polyacrylamide with cationic monomers or polyacrylamides modified in accordance with the Mannich reaction.

14. A composition as set forth in one of the preceding claims characterised in that the polyelectrolyte is a cationic polyacrylamide copolymer selected from the copolymers acrylamides/halide, preferably chloride, of diallyldialkylammonium, the copolymers

diaminoalkylmethacrylate/acrylamides and the copolymers dialkylaminoalkylmethacrylates/acrylamides.

15. A composition as set forth in one of the preceding claims characterised in that the cationic polyelectrolyte is used in a proportion of at most 10% and preferably between 0.3% and 8% by weight of said composition.

16. A composition as set forth in one of the preceding claims characterised in that the mineral cation is a polyaluminum chloride and the cationic polyelectrolyte is a copolymer acrylamide/diallyldimethylammonium chloride of a molecular weight of the order of 3.10^6 .

17. A composition as set forth in one of the preceding claims characterised in that the mineral cation and the polyelectrolyte are used in such a way that the mineral cation/cationic polyelectrolyte molar ratio is between 1.10^2 and 8.10^6 , in particular between 1.10^3 and 8.10^6 .

18. A composition as set forth in claim 17 characterised in that when the mineral cation is polyaluminum chloride and the polyelectrolyte, a copolymer acrylamide/diallyldimethylammonium chloride, the mineral cation/cationic polyelectrolyte weight ratio is between 0.1 and 15 and more particularly between 0.1 and 10.

19. Use of a composition as set forth in one of claims 1 through 18 for the treatment of aqueous media, in particular waste, urban or industrial water.

20. Use of a composition as set forth in one of claims 1 through 18 for the treatment of biological sludges from the purification of dirty or waste water, for the purposes of dehydration thereof.

(12) DEMANDE INTERNATIONALE PUBLIÉE EN VERTU DE LA TRAITÉ DE COOPÉRATION
EN MATIÈRE DE BREVETS (PCT)

(19) Organisation Mondiale de la Propriété
Intellectuelle
Bureau international



(43) Date de la publication internationale
29 mars 2001 (29.03.2001)

PCT

(10) Numéro de publication internationale
WO 01/21532 A1

(51) Classification internationale des brevets⁷: C02F 1/56, 1/52

(74) Mandataire: JACOBSON, Claude; Cabinet Lavoix, 2, place d'Estienne d'Orves, F-75441 Paris Cedex 09 (FR).

(21) Numéro de la demande internationale:
PCT/FR00/02610

(81) États désignés (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CR, CU, CZ, DE, DK, DM, DZ, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW.

(22) Date de dépôt international:
20 septembre 2000 (20.09.2000)

(84) États désignés (régional): brevet ARIPO (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZW), brevet eurasien (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), brevet européen (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), brevet OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).

(25) Langue de dépôt:
français

Publiée:

— Avec rapport de recherche internationale.

En ce qui concerne les codes à deux lettres et autres abréviations, se référer aux "Notes explicatives relatives aux codes et abréviations" figurant au début de chaque numéro ordinaire de la Gazette du PCT

(30) Données relatives à la priorité:
99/11747 20 septembre 1999 (20.09.1999) FR

(71) Déposant (pour tous les États désignés sauf US): RHO-DIA CHIMIE [FR/FR]; 25, quai Paul Doumer, F-92408 Coubevoie Cedex (FR).

(72) Inventeurs; et

(75) Inventeurs/Déposants (pour US seulement): PESCHER, Yvette [FR/FR]; 6, rue de la Mégisserie, F-92220 Bagneux (FR). BAVOUZET, Bruno [FR/FR]; 71, rue de la Condamine, F-75017 Paris (FR). RAFFARD, Michèle [FR/FR]; 36, rue de Picpus, F-75012 Paris (FR).



(54) Title: COMPOSITION USEFUL FOR CONDITIONING SLUDGE DERIVED FROM THE TREATMENT OF AN AQUEOUS MEDIUM AND USES THEREOF

WO 01/21532 A1

(54) Titre: COMPOSITION UTILE POUR LE CONDITIONNEMENT DES BOUES ISSUES DU TRAITEMENT DE MILIEUX AQUEUX ET SES APPLICATIONS

(57) Abstract: The invention concerns a composition useful for conditioning sludge obtained by mixing an invert emulsion containing at least a cationic polyelectrolyte with an invert emulsion or an aqueous solution containing at least a mineral cation with a charge not less than two. The invention also concerns the corresponding applications.

(57) Abrégé: La présente invention concerne une composition utile pour le conditionnement des boues obtenue par mélange d'au moins une émulsion inverse contenant au moins un polyélectrolyte cationique avec une émulsion inverse ou une solution aqueuse contenant au moins un cation minéral de charge supérieure ou égale à deux. Elle a également pour objet les applications correspondantes.

10/03/82 34

114

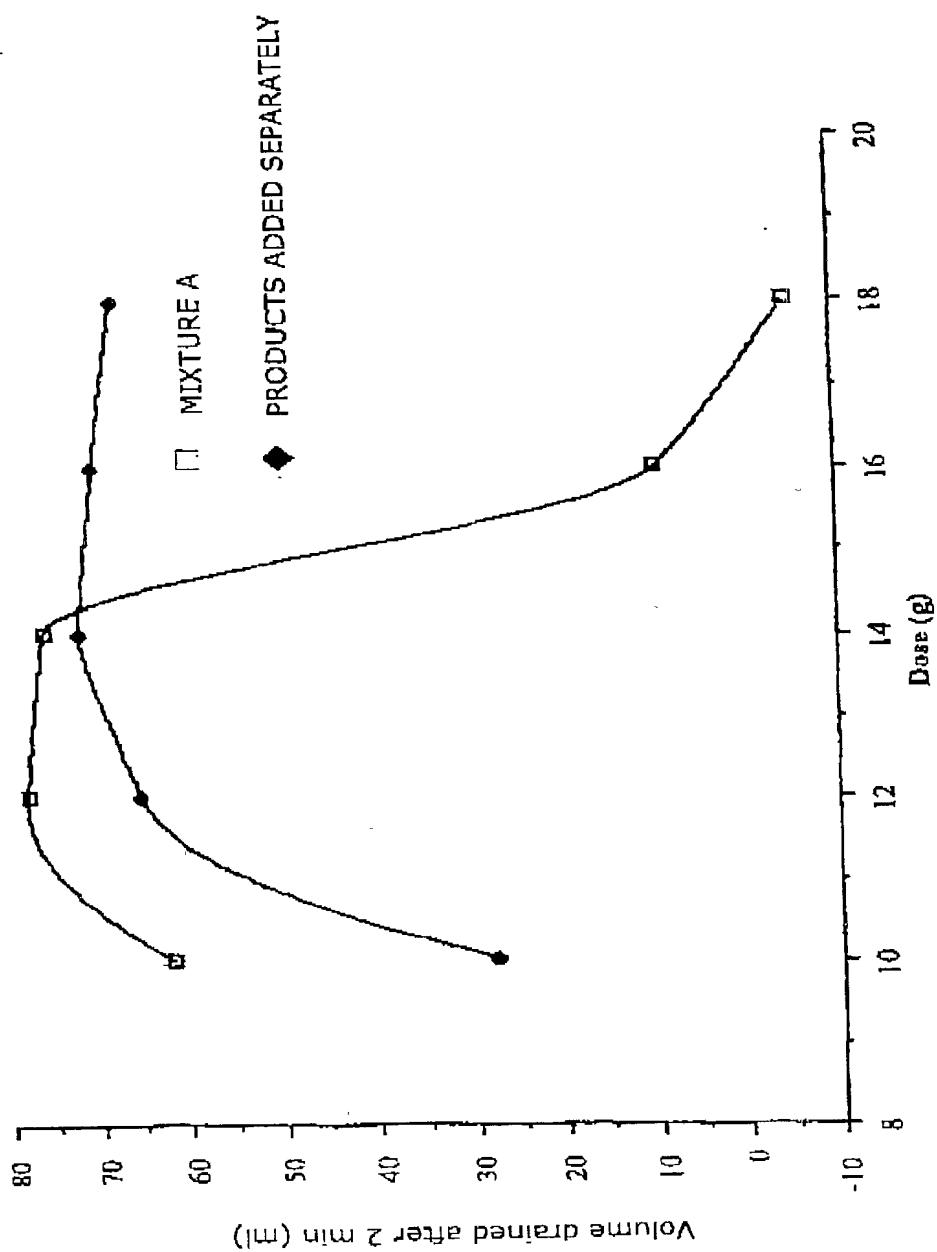


FIG. 1

10/09/234

2/4

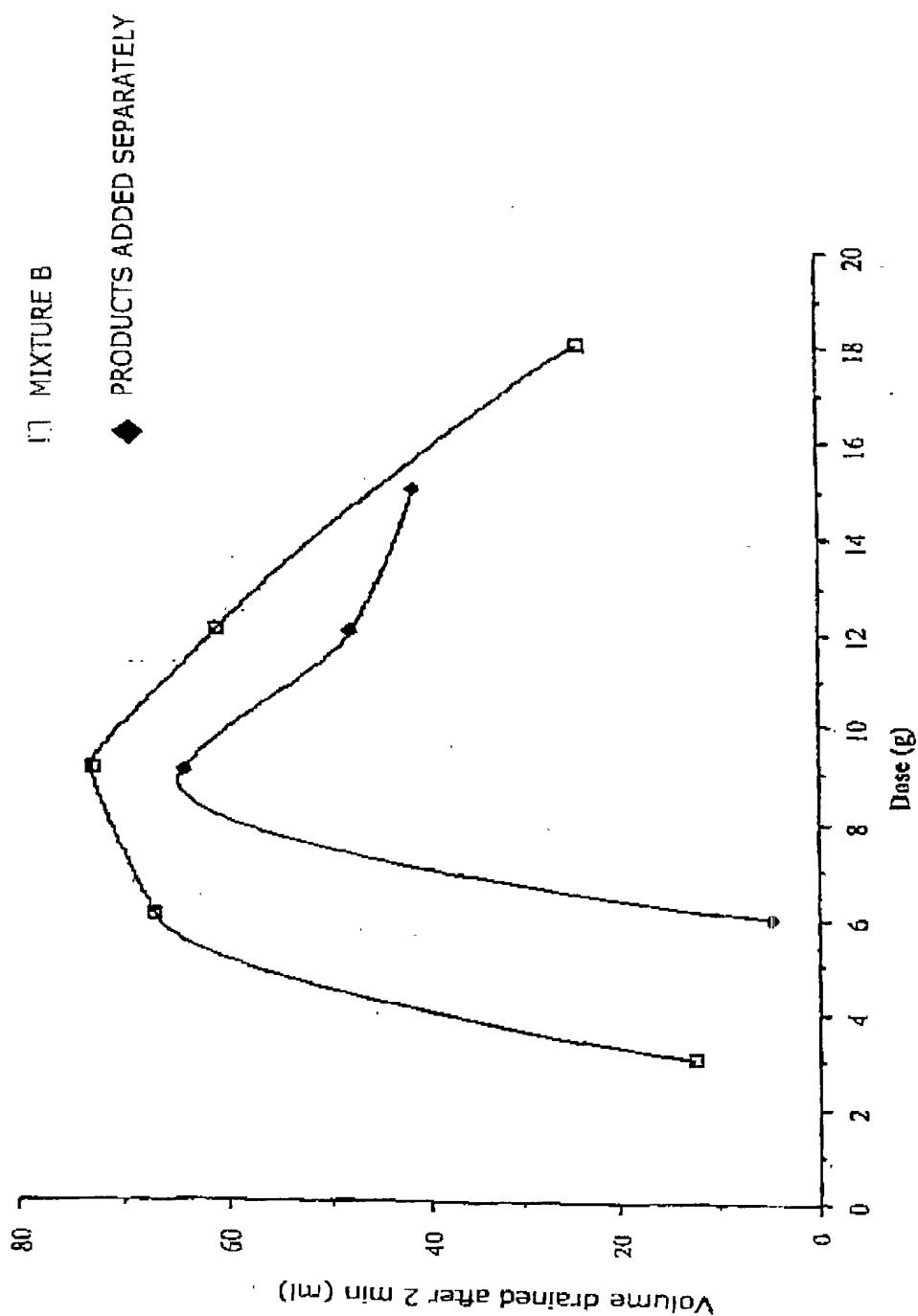


FIG.2

10/08/234

3/4

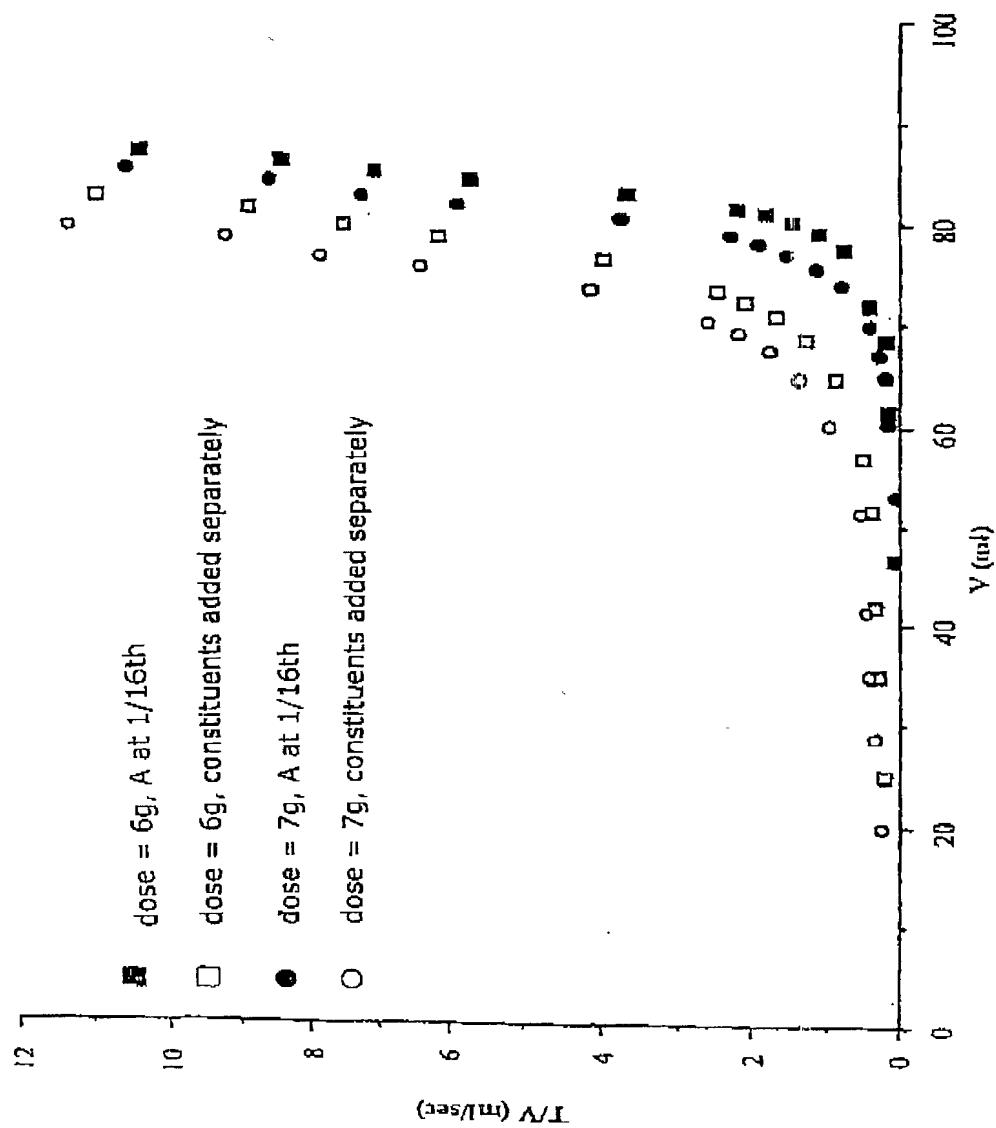


FIG.3

10/08/234

4/4

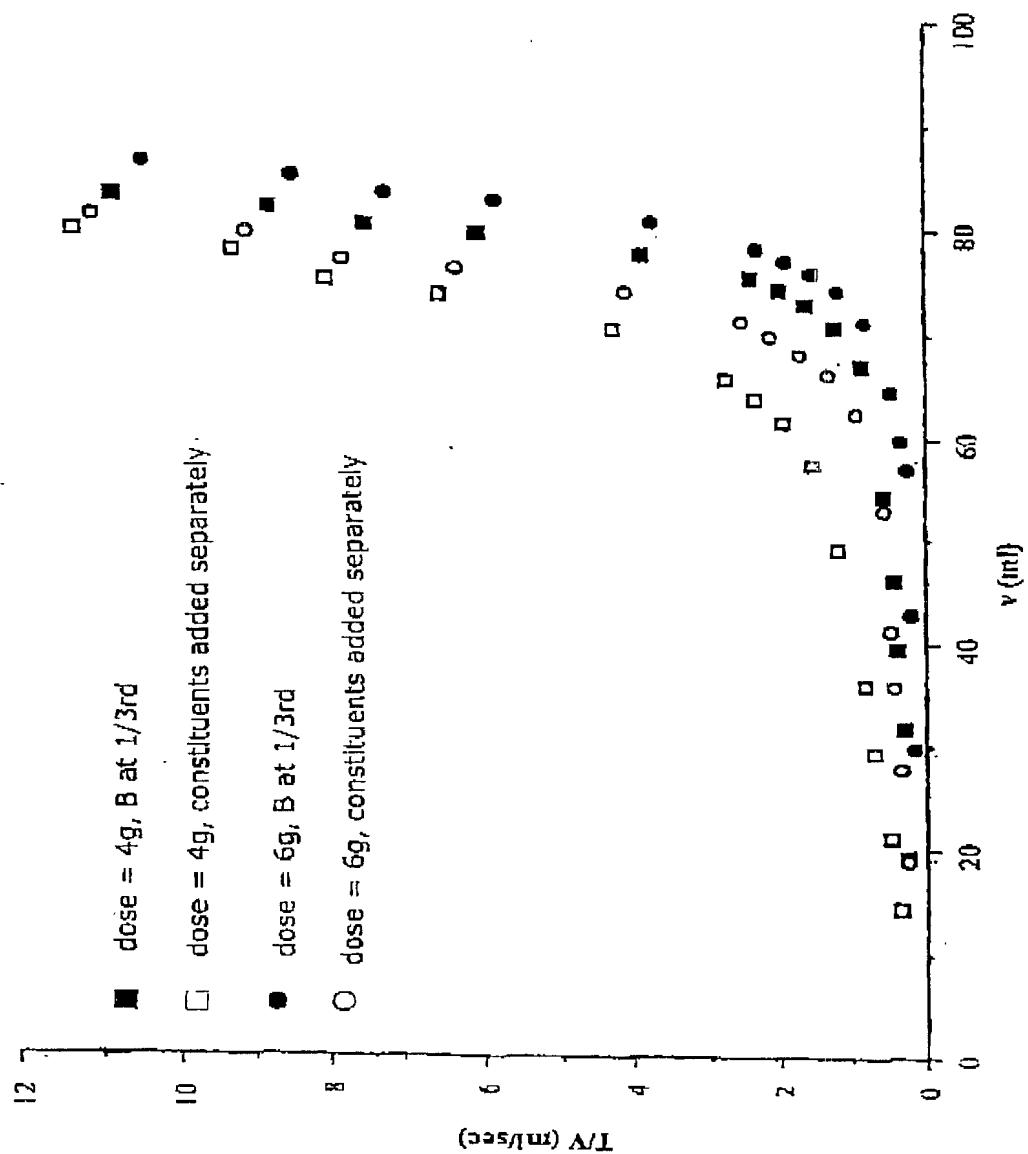


FIG.4

TOTAL P.05

BEP02/ 0265

84G

FR 99 00767

#5

**COMBINED DECLARATION AND POWER OF ATTORNEY
FOR UTILITY PATENT APPLICATION**

Attorney's Docket No.

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name;

I BELIEVE I AM THE ORIGINAL, FIRST AND SOLE INVENTOR (if only one name is listed below) OR AN ORIGINAL, FIRST AND JOINT INVENTOR (if more than one name is listed below) OF THE SUBJECT MATTER WHICH IS CLAIMED AND FOR WHICH A PATENT IS SOUGHT ON THE INVENTION ENTITLED:

Composition useful for conditioning sludge from the treatment of aqueous
media and uses thereof.

the specification of which

(check one)

is attached hereto;

was filed on 20.09.2000 as

Application No. PCT/FROO/02610

and was amended on _____;
(if applicable)

I HAVE REVIEWED AND UNDERSTAND THE CONTENTS OF THE ABOVE-IDENTIFIED SPECIFICATION, INCLUDING THE CLAIMS, AS AMENDED BY ANY AMENDMENT REFERRED TO ABOVE;

I ACKNOWLEDGE THE DUTY TO DISCLOSE TO THE OFFICE ALL INFORMATION KNOWN TO ME TO BE MATERIAL TO PATENTABILITY AS DEFINED IN TITLE 37, CODE OF FEDERAL REGULATIONS. Sec. 1.56 (as amended effective March 16, 1992);

I do not know and do not believe the said invention was ever known or used in the United States of America before my or our invention thereof, or patented or described in any printed publication in any country before my or our invention thereof or more than one year prior to said application; that said invention was not in public use or on sale in the United States of America more than one year prior to said application; that said invention has not been patented or made the subject of an inventor's certificate issued before the date of said application in any country foreign to the United States of America on any application filed by me or my legal representatives or assigns more than twelve months prior to said application;

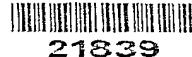
I hereby claim foreign priority benefits under Title 35, United States Code Sec. 119 and/or Sec. 365 of any foreign application(s) for patent or inventor's certificate as indicated below and have also identified below any foreign application for patent or inventor's certificate on this invention having a filing date before that of the application(s) on which priority is claimed:

COMBINED DECLARATION AND POWER OF ATTORNEY		Attorney's Docket No.
---	--	-----------------------

COUNTRY/INTERNATIONAL	APPLICATION NUMBER	DATE OF FILING (day, month, year)	PRIORITY CLAIMED
FRANCE	99 11747	20.09.1999	YES <u>X</u> NO _____
			YES <u> </u> NO _____

I hereby appoint the following attorneys and agent(s) to prosecute said application and to transact all business in the Patent and Trademark Office connected therewith and to file, prosecute and to transact all business in connection with international applications directed to said invention:

William L. Mathis	17,337	R. Danny Huntington	27,903	Gerald F. Swiss	30,113
Robert S. Swecker	19,885	Eric H. Weisblatt	30,505	Charles F. Wieland III	33,096
Plaron N. Mandros	22,124	James W. Peterson	26,057	Bruce T. Wieder	33,815
Benton S. Duffett, Jr.	22,030	Teresa Stanek Rea	30,427	Todd R. Walters	34,040
Norman H. Stepno	22,716	Robert E. Krebs	25,885	Ronni S. Jillions	31,979
Ronald L. Grudziecki	24,970	William C. Rowland	30,888	Harold R. Brown III	36,341
Frederick G. Michaud, Jr.	26,003	T. Gene Dillahunt	25,423	Allen R. Baum	36,086
Alan E. Kopecky	25,813	Patrick C. Keane	32,858	Steven M. duBois	35,023
Regis E. Slutter	26,999	B. Jefferson Boggs, Jr.	32,344	Brian P. O'Shaughnessy	32,747
Samuel C. Miller, III	27,360	William H. Benz	25,952	Kenneth B. Leffler	36,075
Robert G. Mukai	28,531	Peter K. Skiff	31,917	Fred W. Hathaway	32,236
George A. Hovanec, Jr.	28,223	Richard J. McGrath	29,195		
James A. LaBarre	28,632	Matthew L. Schneider	32,814		
E. Joseph Gess	28,510	Michael G. Savage	32,596		



21839

and: Norman H. Stepno

Address all correspondence to:



Norman H. Stepno, Esquire
BURNS, DOANE, SWECKER & MATHIS, L.L.P.
P.O. Box 1404
Alexandria, Virginia 22313-1404

21839

Address all telephone calls to: _____ at (703) 836-6620.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

FULL NAME OF SOLE OR FIRST INVENTOR <u>PESCHER Yvette</u>	SIGNATURE	DATE <u>02.04.2002</u>
RESIDENCE <u>6, rue de la Mégisserie-92220 BAGNEUX- FRANCE</u>		CITIZENSHIP <u>French</u>
POST OFFICE ADDRESS <u>same as above</u>		
FULL NAME OF SECOND JOINT INVENTOR, IF ANY <u>BAVOUZET Bruno</u>	SIGNATURE	DATE <u>02.04.2002</u>
RESIDENCE <u>71, rue La Condamine - 75017 PARIS - FRANCE</u>		CITIZENSHIP <u>French</u>
POST OFFICE ADDRESS <u>same as above</u>		

Attorney's Docket No.

COMBINED DECLARATION AND POWER OF ATTORNEY

300 FULL NAME OF THIRD JOINT INVENTOR, IF ANY RAFFARD Michèle		SIGNATURE <i>Raffard</i>	DATE 02.04.2002
RESIDENCE 36, rue de Picpus - 75012 PARIS - FRANCE		CITIZENSHIP French	
POST OFFICE ADDRESS same as above			
FULL NAME OF FOURTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF FIFTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SIXTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF SEVENTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF EIGHTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF NINTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			
FULL NAME OF TENTH JOINT INVENTOR, IF ANY		SIGNATURE	DATE
RESIDENCE		CITIZENSHIP	
POST OFFICE ADDRESS			